ELECTRONIC ANNEX EA1: RATES OF CRYSTAL NUCLEATION AND GROWTH ESTIMATED BY AN ARRHENIUS-TYPE TEMPERATURE DEPENDENCE

If we assume that the rates of nucleation and growth can be approximated by an Arrhenius-type temperature dependence of the form $A_0 \cdot \exp(\frac{-E_{Act}}{R \cdot T})$ where A_0 is the pre-exponential factor and E_{Act} is the activation energy, then the rate constants for nucleation (K_N) and growth (K_G) can be expressed as:

$$K_N = A_N \cdot exp\left(\frac{-E_N}{R \cdot T}\right) \qquad K_G = A_G \cdot exp\left(\frac{-E_G}{R \cdot T}\right) \tag{1}$$

At low to moderate temperatures the $R \cdot T$ term in the denominator in each exponent is typically small compared to the respective activation energies, E_N and E_G, so that the exponential terms dominated the respective pre-expontential factors in determining the rate constant. Furthermore since the activation energy for nucleation is typically greater than that for growth, i.e., $E_N > E_G$, it follows that $exp\left(\frac{-E_N}{R \cdot T}\right) \ll exp\left(\frac{-E_G}{R \cdot T}\right)$. As a result at these temperatures the rate of growth is faster than the rate of nucleation and the formation of product from reactant is characterized by relatively few large crystals. Conversely, at higher temperatures where the $R \cdot T$ term becomes significant so that the reaction rates for nucleation and growth become dominated by the respective pre-exponential terms A_N and A_G. If, as is typically the case, $A_N > A_G$ then the rate of nucleation is faster than of growth and the reactant phase is characterized by a relatively large numbers of small crystals.